

Behavior of a polymer chain in a critical binary solvent

Michael Stapper and Thomas A. Vilgis

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany
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We present a field-theoretic renormalization group analysis of a polymer chain immersed in a binary good solvent close to its critical demixing point. We first show that this problem can be mapped on a bicritical field theory, i.e. a $(\Phi^2)^2$ -model with a mass anisotropy. This implies that the end-to-end distance of the polymer is now controlled by a new critical exponent ν_B related to the quadratic mass anisotropy operator B . To show this we solve the RG equation and calculate explicitly the exponents and the mean end-to-end length of the chain.

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In this paper we consider the critical behavior of a polymer chain in a critical fluid [1]. This problem is quite poorly understood, because its a coupled system with two macroscopic length scales. The physics is determined by an interplay of the chain length and the correlation length of the critical fluid, which may undergo a phase separation at a certain temperature. The polymer in solution and the critical fluid are separately successfully described by scaling and renormalization group theories. The separation of microscopic and macroscopic length scales leads there to universality. That means the main properties of the system are independent of microscopic details, which only change prefactors in the physical quantities and make analysis of experimental results, at least in their limiting behavior straightforward. We will show that also for our coupled system the application of the RG is possible and yields a description of the conformation of the chain. First insight beyond mean field theory was brought in by Brochard and de Gennes [2] by the use of scaling theory and by the simulation of Magda et al [3], but still there is a lack of a quantitative investigation of the chain conformation near the consolute point of the solvent. The start point of such an investigation is the settled up field theory by Vilgis et al [4].

The polymer chain of configuration $\mathbf{R}(s)$ is modeled by an Edwards-Wiener functional [5]

$$\mathcal{H}_0 = \frac{d}{2l^2} \int_0^L ds \left(\frac{\partial \mathbf{R}(s)}{\partial s} \right)^2 + v \int_0^L \int_0^L ds ds' \delta(\mathbf{R}(s) - \mathbf{R}(s')) \quad , \quad (1)$$

where s is the dimensionless contour variable, l the Kuhn segment length, d the space dimension, v the parameter of the bare short ranged excluded volume interaction, N is the number of segments and $L = lN$ the contour length of the chain. The reduced Hamiltonian of the fluid can be given in terms of three short range pair-potentials between the good solvent molecules

$$H_f = \sum_{\sigma, \tau} \sum_{i, j} V^{\sigma\tau} (\mathbf{r}_i^\sigma - \mathbf{r}_j^\tau) \quad (2)$$

where $\sigma, \tau = 1, 2$ and i, j label the molecules. The interaction between the chain and the fluid is described as

$$\mathcal{H}_i = \int_0^L ds \sum_{\sigma=1,2} \sum_j v_{m\sigma} \delta(\mathbf{R}(s) - \mathbf{r}_j^\sigma) \quad , \quad (3)$$

where $v_{m\sigma}$ characterizes the short range excluded volume interaction between the monomers and the different species of the fluid. If their solvent quality is slightly different, that means $v_{m1} > v_{m2}$ or $v_{m1} < v_{m2}$, there is preferential affinity, the chain is likely to be surrounded by solvent 2 or solvent 1. After the use of collective density fields [4] for the fluid and the chain we get the equivalent complete field theoretical Hamiltonian

$$\mathcal{H} = \int d^d r \left\{ \frac{1}{2}(\nabla\phi(r))^2 + \frac{1}{2}y_0\phi^2(r) + \frac{1}{2}(\nabla\psi(r))^2 + \frac{1}{2}\tau_0\psi^2(r) + \frac{w_0}{2}\phi^2(r)\psi + \frac{g_1}{4!}(\phi^2(r))^2 + \frac{g_2}{4!}\psi^4(r) + 2\frac{g_3}{4!}\phi^2(r)\psi^2(r) \right\} . \quad (4)$$

The polymer field ϕ is an \tilde{M} component field with $\tilde{M} \rightarrow 0$ after the evaluation of the perturbation expansion. The quantity ϕ^2 is related to the monomer density. This follows from the well known de Gennes transformation. Whereas ψ is a scalar field which describes the relative concentration fluctuations of one of the fluid constituents. The term $\phi^2\psi^2$ originates from the incompressibility condition [4] and is important for the physics: In the case of preferential affinity ($w_0 > 0$) it re-swells the chain again in the critical region of the consolute point [2,3]. Whereas in the case of no preferential affinity it is the lowest order coupling between fluid and polymer. It is interesting to note that the same Hamiltonian but with an imaginary coupling w_0 appears in the modeling of a single screened polyelectrolyte chain, i.e. a Debye Hückel chain with corrections [8].

In the following we consider the case with no preferential affinity, i.e. the cubic coupling $w_0 = 0$. We may write the Hamiltonian as one with a composite $M = \tilde{M} + 1$ component field, with $M \rightarrow 1$ due the polymer lines. The fixed point of such a system is for $M < 4$ the Heisenberg fixed point with all corresponding renormalized quartic couplings equal $u_1^* = u_2^* = u_3^* = u^*(M)$ [7]. Due to universality we are allowed to set these couplings already equal in the original (renormalized) Hamiltonian [7] and we get

$$\mathcal{H} = \int d^d r \left\{ \frac{1}{2}(\nabla\Phi(r))^2 + \frac{1}{2}y_0\phi^2(r) + \frac{1}{2}\tau_0\psi^2(r) + \frac{u_0}{4!}(\Phi^2(r))^2 \right\} , \quad (5)$$

with $\Phi = (\phi, \psi)$. This is exactly the Hamiltonian of a bicritical field theory and well investigated by Amit and Goldschmidt [6], but now with y_0 as a monomer chemical potential, an inverse Laplace variable. To analyze the general behavior of the end to end distance, we use the so called soft expansion. That means we write (5) in the form [6],

$$\mathcal{H} = \int d^d r \left\{ \frac{1}{2}(\nabla\Phi(r))^2 + \frac{1}{2}t_0\Phi^2(r) + \frac{u_0}{4!}(\Phi^2(r))^2 - \frac{g_0}{2}B(r) \right\} , \quad (6)$$

with the definitions

$$\begin{aligned} B(r) &= 1/M ((M-1)\psi^2(r) - \phi^2(r)) \\ t_0 &= 1/M(\tau_0 + (M-1)y_0) \\ g_0 &= \tau_0 - y_0 \quad . \end{aligned} \quad (7)$$

The advantage of this splitting is that Φ^2 and B are orthogonal under renormalization, that means divergences which are generated by Φ^2 (B) insertions in vertex functions are absorbed completely by the corresponding counterterms of Φ^2 (B) and these counterterms do not mix with each other under renormalization. We calculate the new exponent ν_B which is given by the anomalous dimension of the operator B corresponding due to the limit $M \rightarrow 1$ to the monomer density. The other exponents η , ν and the β -function are the usual Heisenberg ones, which is obvious in dimensional regularization [7] (the masses g_0 and t_0 are then allowed to set to zero). The upper critical dimension $d_c = 4$ follows from a dimensional analysis of (6) as for the symmetric Heisenberg model with $g_0 = 0$. We show that

$$\begin{aligned} \nu_B &= 1/(2 - \gamma_B) \\ &= (1 + \epsilon/9 + O(\epsilon^2))/2 \quad , \end{aligned} \quad (8)$$

and the cross over exponent is

$$\begin{aligned} \phi &= \nu/\nu_B \\ &= 1 + \epsilon/18 + O(\epsilon^2) \quad , \end{aligned} \quad (9)$$

and $\nu = (1 + \epsilon/6 + O(\epsilon^2))/2$, consistent with [6]. But the soft expansion (6) is only useful for general considerations like the solution of RG-equations. Whereas for perturbation expansions of polymer quantities it is not possible to use (6), because an expansion in g_0 is an expansion in an inverse Laplacian and therefore all back transformed contributions are order by order zero.

Now we perform a general renormalization group analysis of our model given by equation (6). Our goal is to calculate the end to end distance of the polymer

$$\begin{aligned} \langle R^2 \rangle &= -T_{\mathcal{L}}^{-1} \left(\partial_{q^2} \tilde{G}^{(2)}(q)|_{q=0} \right) / T_{\mathcal{L}}^{-1} \left(\tilde{G}^{(2)}(q=0) \right) \\ &= D(u) F(\tau, \mathcal{L}) \quad , \end{aligned} \quad (10)$$

here is $G^{(2)}(r) = \int d^d q / (2\pi)^d e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{G}^{(2)}(q) = \mathcal{N} \int \mathcal{D}\Phi \mathcal{D}\psi \Phi(r) \Phi(0) e^{-H(\Phi, \psi)}$, the propagator of the polymer, \mathcal{N} is a normalization constant, $T_{\mathcal{L}}^{-1}$ is the inverse Laplacian with respect to (wrt) $\mathcal{L} = 2lL = 2l^2 N/d$, $\tilde{G}^{(2)}(q)$ is the Fourier transform of the renormalized chain propagator and $D(u)$ is a non universal constant.

Due to the particular choice of B we have a separate (diagonal) renormalization scheme [6], which expresses the bare parameters in terms of their renormalized ones:

$$t_0 = Z_{\Phi^2} t, \quad g_0 = Z_B g, \quad u_0 = Z_u u S_d \mu^\epsilon \quad (11)$$

Here μ^{-1} is an external length scale and $S_d = \Omega_d / (2\pi)^d$ with Ω_d the volume of the unit sphere.

We denote an N point vertex function as $\Gamma^{(N)}$ and a composite one with N points and L , Φ^2 and K , B insertions as $\Gamma^{(N, L, K)}$. The wave-function renormalization factor is calculated by expressing the renormalized vertex functions in terms of the bare ones as

$$\Gamma_R^{(N)} = Z_\Phi^{N/2} \Gamma^{(N)} \quad . \quad (12)$$

Whereas the renormalization of the composite ones give similar [6]

$$\Gamma_R^{(N, L, K)} = Z_\Phi^{N/2} Z_{\Phi^2}^L Z_B^K \Gamma^{(N, L, K)} \quad . \quad (13)$$

The renormalization group equations follow from an variation wrt the external scale μ and are given by

$$[\mu \partial_\mu + \beta \partial_u + \gamma_{\Phi^2} \tau \partial_\tau + \gamma_B g \partial_g - \gamma_\Phi N/2] \Gamma_R^{(N)} = 0 \quad , \quad (14)$$

with the Wilson-functions $\beta = \mu du/d\mu$, $\gamma_{B/\Phi^2} = -\beta(\partial \ln Z_{B/\Phi^2} / \partial u)$ and $\gamma_\Phi = \beta(\partial \ln Z_\Phi / \partial u)$. The equivalent form in polymer variables is obtained by an inverse Laplace Transformation with partial integration wrt g . The vertex functions are calculated using a dimensional regularized scheme with minimal subtraction of poles [7]. The vertex function $\Gamma^{(2)}$ yields the wave function renormalization $Z_\Phi = 1 + O(u^2)$. The determination of Z_u is obtained by the $1/\epsilon$ -part of $\Gamma^{(4)}$ and is

$$Z_u = 1 + \frac{3u}{2\epsilon} + O(u^2) \quad , \quad (15)$$

from which follows the β -function the zero of which yields the infra-red stable fixed point $u^* = 2\epsilon/3 + O(\epsilon^2)$. An evaluation of $\Gamma^{(2, 1, 0)}$ yields

$$Z_{\Phi^2} = 1 + \frac{u}{2\epsilon} + O(u^2) \quad , \quad (16)$$

whereas $\Gamma^{(2, 0, 1)}$ yields

$$Z_B = 1 + \frac{u}{3\epsilon} + O(u^2) \quad . \quad (17)$$

From the above equations we now obtain the exponents due to the relations [6,7]

$$\eta = \gamma_\Phi(u^*, \epsilon), \quad \nu^{-1} - 2 = \gamma_{\Phi^2}(u^*, \epsilon), \quad \nu_B^{-1} - 2 = \gamma_B(u^*, \epsilon) \quad , \quad (18)$$

which yield the exponents given in equations (8) and (9). Our results are to order ϵ , with corrections of the order of ϵ^2 .

To see the scaling form of $\langle R^2 \rangle$ we need to solve the RG equation for the Fourier transformed chain partition function $\tilde{Z}_R^{(2)}(q) = T_{\mathcal{L}}^{-1}(\tilde{G}^{(2)}(q))$ which is given by

$$[\mu\partial_\mu + \beta\partial_u + \gamma_{\Phi^2}\tau\partial_\tau - \gamma_B L\partial_L + \gamma_\Phi + \gamma_B]\tilde{Z}_R^{(2)}(q, \tau, L, u, \mu) = 0 \quad , \quad (19)$$

The solution is obtained by the method of characteristics [7] and gives the scaling form of $\langle R^2 \rangle$ to be [9]

$$\begin{aligned} F(\tau, \mathcal{L}) &= \mathcal{L}^{2\nu_B} \tilde{F}(\tau \mathcal{L}^{\nu_B/\nu}, u^*) \\ &= |\tau|^{-2\nu} \tilde{F}_\pm(\mathcal{L}|\tau|^{\nu/\nu_B}, u^*) \end{aligned} \quad (20)$$

We see that in the above equations the cross over exponent ϕ is appeared. Here \pm denotes $T > T_c$ and $T < T_c$, respectively.

Now we calculate the explicit form of the scaling function of the end to end distance $\langle R^2 \rangle$ in case of $\tau \rightarrow 0$ ($T \geq T_c$) and $\mathcal{L} \rightarrow \infty$ so that $\tau\mathcal{L}$ stays finite. We need the general matrix renormalization scheme, because no soft expansion wrt the monomer chemical potential is possible. We have to use instead of equation (11) for the vertex renormalization

$$\begin{aligned} y_0 &= Z_{21}\tau + Z_{22}y \\ \tau_0 &= Z_{11}\tau + Z_{12}y \quad . \end{aligned} \quad (21)$$

These Z -factors are simply given by the renormalization of the corresponding vertex functions with zero momentum for the polymer and the fluid $\tilde{\Gamma}_{22}^{(2)}(k=0)$ and $\tilde{\Gamma}_{11}^{(2)}(k=0)$ which fix the values of Z_{21} and Z_{22} and Z_{11} and Z_{12} . They are given to order 1-Loop in the figures 1 and 2.

$$\tilde{\Gamma}_{22}(k) = \frac{2}{2} + \frac{2}{2} + \frac{2}{2} + O(u^2)$$

FIG. 1. The diagrams for the polymer $\Gamma_{22}^{(2)}$. A line with the number 2 corresponds to a free polymer propagator $(k^2 + y)^{-1}$, a line with 1 to a fluid propagator $(k^2 + \tau)^{-1}$ and dotted line to a interaction vertex $u/4!$. Note that we do not include external legs and evaluate the graphs at $k=0$ for the vertex function. The chain propagator $G^{(2)}$ is also calculated using these graphs including external legs and with k finite.

$$\tilde{\Gamma}_{11}(k) = \frac{1}{1} + \frac{1}{1} + \frac{1}{1} + O(u^2)$$

FIG. 2. The diagrams for the fluid $\Gamma_{11}^{(2)}$

The evaluation of their Feynman diagrams yield $Z_{21} = \frac{u}{6\epsilon} + O(u^2)$, $Z_{22} = 1 + \frac{u}{3\epsilon} + O(u^2)$, $Z_{11} = 1 + \frac{u}{2\epsilon} + O(u^2)$ and $Z_{12} = 0$, in the polymer limit $M \rightarrow 1$.

The corresponding RG equation for $\tilde{\Gamma}_{22R}^{(2)}$ is then

$$[\mu\partial_\mu + \beta\partial_u + \kappa_\tau\tau\partial_\tau + (\kappa_{21}\tau + \kappa_{22}y)\partial_y - \gamma_\Phi]\tilde{\Gamma}_{22R}^{(2)} = 0 \quad , \quad (22)$$

and follows from a variation wrt the external length μ^{-1} . The new coefficients are $\kappa_\tau = -\beta\partial_u \ln Z_{11}$, $\kappa_{22} = -\beta\partial_u \ln Z_{22}$ and $\kappa_{21} = -1/Z_{22}(\beta\partial_u Z_{21} - Z_{21}\kappa_\tau)$.

After an inverse Laplace transformation wrt y of the RG equation for the propagator $\tilde{G}^{(2)} = 1/\tilde{\Gamma}^{(2)}$ we get for the 2-point chain partition function

$$[\mu\partial_\mu + \beta\partial_u + \tau\kappa_\tau\partial_\tau - \kappa_{22}L\partial_L + \gamma_\Phi - \kappa_{22} - \kappa_{21}\tau L] \tilde{Z}_{22R}^{(2)} = 0 \quad . \quad (23)$$

With the use of characteristics as mentioned after (19) we find the solution of (23) and it turns out the same scaling form for $\langle R^2 \rangle$ as in the soft expansion (20) because both renormalization schemes are equivalent. But the critical exponents are now defined as $1/\nu_B = 2 - \kappa_{22}(u^*)$, $1/\nu = 2 - \kappa_\tau(u^*)$ and $\eta = \gamma_\Phi(u^*)$. Because the solution of the general vertex matrix renormalization has to be consistent with the diagonal (soft expansion) scheme of (19), it follows that $Z_{22} \equiv Z_B$ and $Z_{11} \equiv Z_{\Phi^2}$ to all orders in u . But we need the matrix scheme for the analysis of the explicit loop-expansion: By using the flow equations from the method of characteristics similar as in the calculation of the equation of state for magnetic systems [7] we get from the expansion of $\tilde{\Gamma}_{22}^{(2)}$ finally the explicit result valid to order ϵ

$$\langle R^2 \rangle \sim \mathcal{L}^{2\nu_B} \quad . \quad (24)$$

This scaling form is consistent with the general result (20).

Now we express our renormalized quantities by the original bare ones and find that

$$\langle R^2 \rangle = D(u) l^2 N^{2\nu_B} \quad , \quad (25)$$

with a non universal constant $D(u)$ [9]. There is in 1-loop order no explicit temperature dependence of the demixing binary solvent but we have the implicit condition that $\tau_0 N l^2$ is finite in the critical limit.

To summarize: we found that in the critical region the demixing tendency of the fluid yields, if the number of monomers $N \rightarrow \infty$ and the critical temperature deviation of the fluid $\tau_0 \rightarrow 0$ such that $lN\tau_0$ stays finite, to a smaller chain size than in each of the good solvent components separately. This is because the new exponent ν_B is less than the self avoiding walk exponent $\nu_0 = (1 + \epsilon/8 + O(\epsilon^2))/2$. To get an explicit demixing temperature dependence in the end-to-end distance of the polymer chain a calculation to a higher Loop order is necessary. Now only the exponent ν_B can be found in 2-Loop order in reference [6].

The binary solvent with preferential affinity to the monomers is not tractable by the renormalization group. Due to the induced preferential adsorption the chain likes to be surrounded by the better solvent. This effective long range attraction of the range of the fluid correlation length yields in a specific temperature range to a partly collapsed chain [1–4]. In the RG calculation this manifests in a dominant cubic term in the Hamiltonian which implies an imaginary solution of the β -function [9].

A related problem is a screened polyelectrolyte chain in a demixing binary solvent. The effective attractive interaction induced by the preferential affinity leads then to an effective charge of the monomers [9].

Real systems have preferential affinity. Therefore its interesting to investigate if at least right at the consolute point of the fluid the preferential adsorption term has still significant influence on the (infinite) chain size, because the chain is then again swollen. This could be done by computer-experiments.

Note added: After acceptance of the present paper an experimental study appeared [10] which agrees in several points with our results.

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$$\tilde{\Gamma}_{22}(k) = \frac{\text{---}2\text{---}}{2} \frac{\text{---}2\text{---}}{2} + \frac{\text{---}2\text{---}}{2} \frac{\text{---}\triangle\text{---}}{2} + \frac{\text{---}2\text{---}}{2} \frac{\text{---}\bigcirc\text{---}}{2} + O(u^2)$$

FIG. 3. The diagrams for the polymer $\Gamma_{22}^{(2)}$. A line with the number 2 corresponds to a free polymer propagator $(k^2 + y)^{-1}$, a line with 1 to a fluid propagator $(k^2 + \tau)^{-1}$ and dotted line to a interaction vertex $u/4!$. Note that we do not include external legs and evaluate the graphs at $k = 0$ for the vertex function. The chain propagator $G^{(2)}$ is also calculated using these graphs including external legs and with k finite.

$$\tilde{\Gamma}_{11}(k) = \frac{\text{---}1\text{---}}{1} \frac{\text{---}1\text{---}}{1} + \frac{\text{---}1\text{---}}{1} \frac{\text{---}\triangle\text{---}}{1} + \frac{\text{---}1\text{---}}{1} \frac{\text{---}\bigcirc\text{---}}{1} + O(u^2)$$

FIG. 4. The diagrams for the fluid $\Gamma_{11}^{(2)}$.